

Hierarchically Structured MoO₂/Dopamine-Derived Carbon Spheres as Intercalation Electrodes for Lithium-Ion Batteries

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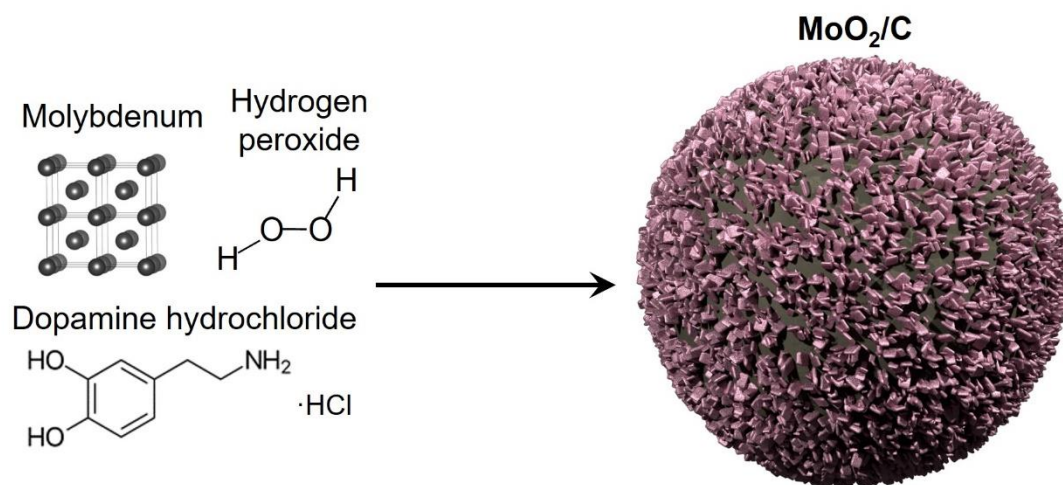
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Abstract:

A hydrogen peroxide initiated sol-gel process involving molybdenum transformation in the presence of dopamine (Dopa) hydrochloride excess produced the metastable precipitate composed of polydopamine (PDopa) spheres coated with dopamine preintercalated molybdenum oxide, (Dopa)_xMoO_y@PDopa. The hydrothermal treatment (HT) of the (Dopa)_xMoO_y@PDopa precursor resulted in the simultaneous carbonization of dopamine and molybdenum reduction generating MoO₂ nanoplatelets distributed and confined on the surface of the dopamine-derived carbon matrix (HT-MoO₂/C). The consecutive annealing (An) of the HT-MoO₂/C sample at 600°C under Ar atmosphere led to the formation of MoO₂ with increased Mo oxidation state and improved structural stability (AnHT-MoO₂/C). Annealing had also further facilitated interaction between the molybdenum-derived and dopamine-derived components resulting in the modification of the carbon matrix confirmed by Raman spectroscopy. Morphology of both materials is best described as dopamine-derived carbon spheres decorated with MoO₂ nanoplatelets. These integrated metal

oxide and carbon structures were tested as electrodes for lithium-ion batteries in the potential window that corresponds to the intercalation mechanism of charge storage. The AnHT-MoO₂/C electrode showed enhanced electrochemical activity, with an initial specific discharge capacity of 260 mAh g⁻¹ and capacity retention of 56% after 50 cycles, as compared to the HT-MoO₂/C electrode which exhibited an initial specific discharge capacity of 235 mAh g⁻¹ and capacity retention of 34% after 50 cycles. The rate capability experiments revealed that the capacity of 93 mAh g⁻¹ and 120 mAh g⁻¹ was delivered by the HT-MoO₂/C and AnHT-MoO₂/C electrodes, respectively, when the current density was increased to 100 mA g⁻¹. The improved specific capacity, electrochemical stability, and rate capability achieved after annealing were attributed to higher crystallinity of MoO₂, increased oxidation state of Mo, and formation of the tighter MoO₂/carbon contact accompanied by the annealing assisted interaction between MoO₂ and dopamine-derived carbon.

Graphical Abstract

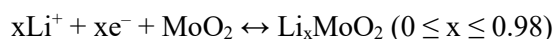


1. Introduction

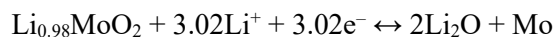
Rechargeable lithium-ion batteries (LIBs) feature high energy density and a long and reliable life span. Their dominance in the portable electronics and expanding electric vehicles market is expected to continue for the next few decades calling for the enrichment of the existing library of materials used in batteries.¹ Transition metal oxides (TMOs) offer versatile structures and chemistries that can be used as electrodes. One of the fundamental requirements for developing TMO electrodes with high-performing energy storage capabilities is fast ion diffusion combined with high electronic conductivity. However, most oxides exhibit poor electron transport. This challenge can be overcome by creating oxide/carbon integrated architectures with an intimate heterointerface. Tight oxide/carbon contact can be achieved through the assembly of dissolved oxide and carbon precursors followed by the treatment at elevated temperatures to induce carbonization and crystallization of the oxide phase.

Molybdenum dioxide (MoO₂) emerged as a promising electrode material for LIBs.²⁻⁴ The lithium charge storage mechanism in MoO₂ consists of two steps:²

Step 1: Intercalation



Step 2: Conversion



The overall MoO₂ theoretical capacity of 838 mAh g⁻¹, corresponding to both steps, is accompanied by the severe volume change leading to poor cyclability. When cycling is limited to the intercalation reaction only, the theoretical capacity is 209 mAh g⁻¹. Nevertheless, bulk MoO₂ electrodes usually exhibit poor kinetics due to their compact crystal structure and poor conductivity of the lithiated Li_{0.98}MoO₂ resulting in unsatisfactory rate capability.^{5,6} Nanostructuring MoO₂ particles can expose more channels for Li⁺ ion diffusion and improve the kinetics of reversible ion intercalation. However large contact resistance remains

a challenge for the electrodes containing MoO₂ nanoparticles. Creating a porous electrode architecture that combines pathways for electron transport, such as carbonaceous species, with nanostructured MoO₂ and intimate oxide/carbon interface is a promising approach to achieve enhanced energy storage properties.^{2,7-9} Carbon-containing structures are also able to effectively prevent the restacking and accommodate volume change of metal oxides. Various nanostructures of MoO₂ and carbon such as MoO₂/C microflowers,² MoO₂ nanopopcorns decorated carbon,⁴ porous MoO₂ nanotubes,¹⁰ and MoO₂ coated with N-doped carbon,¹¹ have been synthesized. For the synthesis of MoO₂/C nanocomposites, typically, MoO₃ nanoparticles are first prepared through hydrothermal treatment followed by subsequent reduction via interaction with a reducing agent such as H₂. While this synthesis strategy has aimed for creating a close MoO₂/C contact, the carbon component was only introduced as carbon nanoparticles during the hydrothermal treatment process or physical mixing after the formation of MoO₃ nanostructures. None of the reported MoO₂/C nanocomposites has been prepared via simultaneous carbonization of the organic precursor molecules and crystallization of MoO₂. Also, most of the reports investigated charge storage characteristics in a potential window covering both intercalation and conversion processes. Little is known about the reversible electrochemical lithium-ion intercalation in MoO₂, while current battery technology is dominated by intercalation batteries.

Chemical preintercalation of organic molecules is a synthetic pathway that can be used to achieve oxide/carbon architectures. In this process, organic molecules are added into a reaction mixture during the sol-gel process for the synthesis of the oxide phase. Hydrothermal treatment and/or annealing of the thus obtained precursor at elevated temperatures leads to carbonization of the organic component and formation of the oxide/carbon heterointerface. Using dopamine hydrochloride, this method was utilized to successfully prepare vanadium oxide/carbon heterostructure that showed enhanced charge storage properties in lithium-ion cells.¹² However, the limited dopamine concentration resulted in only a small fraction of carbon in the product. Further improvement can be achieved by increasing carbon content via enriching the system with dopamine. Increasing the concentration of dopamine in the sol-gel reaction mixture in the presence of an oxidizing agent such as hydrogen peroxide can initiate the polymerization of

the organic molecule. Typically, polymerization of dopamine requires weak alkaline conditions (pH 8.5) and tris (hydroxymethyl) aminomethane (Tris-base) buffer,¹³ and hydrogen peroxide alone cannot support the oxidative polymerization as the oxygen species react with the aromatic rings of dopamine and disrupt the structure formation.¹⁴ Continuation of the polymerization of dopamine in acidic reactions requires hydrothermal processing at temperatures above 160 °C and high pressure.^{15,16} Use of polydopamine for the synthesis of derived carbon materials allows for control over morphology and porosity¹⁷ as well as facilitating the introduction of nitrogen dopants in the structure of the final carbon-containing product which directly improves the conductivity by doping of an additional electron into the delocalized π -system and changing the charge distribution of the surface.^{18,19}

Here, we report a sol-gel process-based synthesis approach leading to the formation of the unique MoO₂/C spheres with porous hierarchical architecture. In these materials, MoO₂ nanoplatelets are integrated onto a dopamine-derived carbon scaffold taking advantage of the excellent self-assembly property and carbonization of dopamine.¹⁷ The sol-gel reaction between metallic molybdenum and hydrogen peroxide is carried out in the presence of the dopamine hydrochloride excess (molar ratio of dopamine : Mo = 1 : 1) leading to the formation of the polydopamine spheres coated with dopamine preintercalated molybdenum oxide, (Dopa)_xMoO_y@PDopa. Transformation of the (Dopa)_xMoO_y@PDopa into hierarchically-structured MoO₂/C spheres is induced by hydrothermal treatment at 220°C. Further evolution of the chemical composition, crystallinity, and morphology of the MoO₂/C nanocomposites is achieved by annealing at 600°C under Ar flow. Electrochemical testing of the Li-ion cells containing HT-MoO₂/C and AnHT-MoO₂/C electrodes in the 1.2 – 3.0 V vs Li/Li⁺ potential window, corresponding to the intercalation mechanism of charge storage, revealed improvements in specific capacity, cycle life and rate capability enabled by the annealing process. Transformation of the dopamine precursor with simultaneous change in the oxidation state of molybdenum leads to the formation of a highly MoO₂/carbon integrated structure that can take advantage of improved conductivity due to the incorporation of carbon and enhanced stability of the crystal structure of the active material. We believe that our synthesis strategy leading to the formation

of MoO₂ nanoplatelets tightly integrated with spherical dopamine-derived carbon matrix is promising for the design of next-generation multifunctional electrode materials for high-performance lithium-ion batteries.

2. Experimental Methods

2.1 Synthesis of (Dopa)_xMoO_y@PDopa, HT-MoO₂/C, An-HT-MoO₂/C, AnHT-MoO₂/C

Dopamine (Dopa) preintercalated molybdenum oxide covered polydopamine (PDopa) spheres, (Dopa)_xMoO_y@PDopa, precursor was synthesized using the modified sol-gel process involving dissolution of metallic Mo in water by addition of hydrogen peroxide.¹² First, 0.95 g of dopamine hydrochloride ((HO)₂C₆H₃CH₂CH₂NH₂·HCl or Dopa·HCl, Alfa Aesar) is dissolved in 7 mL of deionized water. Minimizing the volume of water speeds up the product formation drastically from a few days (15 mL) to only a few hours (7 mL). The procedure is followed by the addition of the stoichiometric amount (0.48 g) of metallic Mo powder (Alfa Aesar) to the solution. The molar ratio of Mo:Dopa was kept at 1:1 to ensure dopamine excess as compared to the previous study where V₂O₅:Dopa molar ratio of 5:1 was used.¹² Hydrogen peroxide (30 wt. % H₂O₂, Alfa Aesar) was added dropwise until all Mo was dissolved; then the temperature of the reaction was set to 60°C. Using the lowest amount of H₂O₂, sufficient for dissolving Mo powder, decreased the time of the product formation. The product precipitate started forming in a few hours and it was allowed to age for 5-7 days in a fume hood at room temperature. The aged product was then filtered and washed with deionized water. The yellow powder, collected after washing, was kept in the freezer at -20 °C overnight followed by freeze drying (0.001 mbar, -84 °C Freezone, Labconco) to remove interlayer water. The produced powder is called the precursor in this study and denoted as (Dopa)_xMoO_y@PDopa.

Carbonization/polymerization was induced using the hydrothermal treatment and/or annealing. First, 300 mg of the (Dopa)_xMoO_y@PDopa precursor, were placed into 12 mL of water in a 23 mL Teflon-lined autoclaves (PARR, Acid Digest Vessel 23 mL) and kept at 220°C for 24 h. The product, which we call HT-MoO₂/C, was filtered, washed with deionized water, and dried at 105°C in air. Annealing of the HT-

MoO₂/C powder at 600°C for 6 h under continuous Ar flow in a tube furnace (Thermcraft Inc.) produced a sample which we call AnHT-MoO₂/C. Alternatively, we annealed the (Dopa)_xMoO_y@PDopa precursor using the same conditions (600°C for 6 h under continuous Ar flow). For consistency, we call this material An-MoO₂/C, however its true chemical composition is revealed in the Results and Discussion section.

2.2 Materials Characterization

The phase composition of the synthesized materials was analyzed using X-ray diffraction (XRD) measurements. XRD patterns were collected in a 2θ range of 5° - 60° with a step size of 0.02° using a Rigaku SmartLab X-ray diffractometer (Japan) with Cu Kα radiation. A Zeiss Supra 50VP (Germany) scanning electron microscope (SEM) was used to characterize particle morphology. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and high-angle annular dark field scanning TEM (HAADF-STEM) images were collected using a JEOL 2100F operated at 200 kV. Samples were suspended in ethanol and drop casted on carbon-supported TEM grids. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q50 (TA Instruments, USA) and was conducted from room temperature to 700°C in air. Further details on the chemical composition of the synthesized materials were gathered via Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy. FTIR spectra were collected from 500 to 4000 cm⁻¹ using a Nicolet 6700 FTIR spectrometer. Raman spectra were obtained from 100 to 2500 cm⁻¹ using a Renishaw inVia Raman microscope (Renishaw, United Kingdom) with 514 nm Ar-ion laser. Mo K-edge fluorescence X-ray absorption spectroscopy (XAS) data were collected at the 7-BM beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory. The synthesized materials were diluted with boron nitride (BN) to achieve optimal transmission. Spectra were collected for reference materials to aid in data interpretation. The collected spectra were background subtracted, aligned, and normalized using the Athena software package. Linear combination fitting (LCF) was completed using spectra for two crystalline end members, MoO₂ and MoO₃ as reference materials to estimate the oxidation state of the synthesized material. Electronic conductivity was evaluated by measuring the sheet resistance of pressed pellets using a Jandel Engineering Ltd. ResTest four-point probe instrument (Jandel Engineering,

United Kingdom) with a 1 mm probe distance. To make uniform pellets and avoid their shattering during preparation or measurement, sample powders were thoroughly ground with 5 wt.% PTFE binder (60 wt.% dispersion in water, Sigma Aldrich). The mixtures were dried at 120 °C overnight to evaporate the water. The dried samples were rolled into a thin film and a small piece of the film was cut and folded. All pellets were pressed by using a Carver press (Carver Inc., USA) at ~80 MPa, and wafer resistivity was measured at currents between 1 and 10 μ A. The pellets used in this measurement had the thickness of 0.145-0.175 mm. The reported conductivity was determined via the following equation:

$$\text{electronic conductivity } (S \text{ cm}^{-1}) = \frac{1}{4.532 \frac{V}{I} t}$$

where V is the measured voltage, I is the applied current, and t is the thickness of the pellets.

2.3 Electrochemical Testing

For making the electrodes, first slurries with 70: 20:10 by weight mixture of active material, carbon black, and a 10 wt. % poly (vinylidene fluoride) (PVDF) as a polymer binder in 1-methyl-2-pyrrolidinone (NMP) were prepared. The electrode films were fabricated by casting the slurries onto an aluminum foil current collector using a doctor blade. The films were air-dried overnight in the fume hood then dried at 105 °C for 12 h in a vacuum oven. 12 mm electrodes were punched out and the electrodes were dried again at 105 °C in the vacuum oven. The electrodes were transferred into an Ar-filled glovebox and used in cell assembly. All electrodes were cycled in a Li-ion system using 2032 type coin cells. The following components were used to assemble the cell: Li metal foil (Alfa Aesar) as the counter/reference electrode, Celgard as the separator, and 1 M LiPF₆ in EC: DEC (BASF LP40) as the electrolyte. Cyclic voltammetry (CV) characterization was performed using a Biologic VMP3 multichannel potentiostat/galvanostat. CV curves were obtained by cycling electrodes in the 1.0–3.0 V potential window with a scan rate of 0.1 mV s⁻¹. Galvanostatic cycling experiments at a current density of 10 mA g⁻¹, rate capability experiments and electrochemical impedance spectroscopy (EIS) were conducted using an Arbin battery testing station

(Arbin Instruments, USA). The rate capability of the synthesized materials was investigated at increasing current densities (10, 20, 50, 100, and then back to 20 mA g⁻¹ for 10 cycles at each current density). EIS measurements were performed by applying an alternating voltage (10 mV) in the frequency range between 10 mHz and 200 kHz at the open circuit voltage.

3. Results and Discussion

The process illustrating our synthesis strategy to prepare integrated MoO₂/C hierarchically structured porous spheres is schematically shown in **Figure 1**. The H₂O₂-triggered sol-gel reaction is used to dissolve metallic molybdenum in the aqueous environment enriched with dopamine. Complex chemical interactions in the reaction mixture involve the formation of the polydopamine spheres coated with the dopamine-preintercalated molybdenum oxide, (Dopa)_xMoO_y@PDopa, which serves as a precursor (**Figure 2a, b**). The (Dopa)_xMoO_y@PDopa precursor is further processed at elevated temperatures through hydrothermal treatment (HT-MoO₂/C), annealing under an inert atmosphere (An-MoO₂/C), and hydrothermal treatment followed by the annealing under an inert atmosphere (AnHT-MoO₂/C) (**Figure 1**).

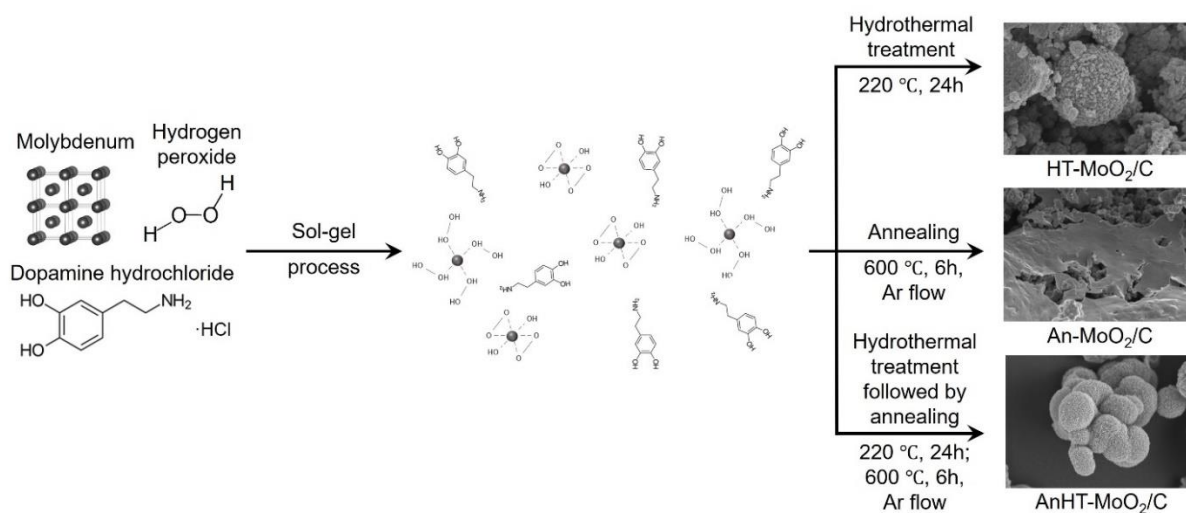


Figure 1. Schematic illustration of the synthesis process involving sol-gel reaction between metallic molybdenum and hydrogen peroxide in the presence of dopamine hydrochloride. The product of the sol-gel reaction was hydrothermally treated, annealed, and hydrothermally treated followed by annealing. SEM images show the morphology of the as-synthesized materials.

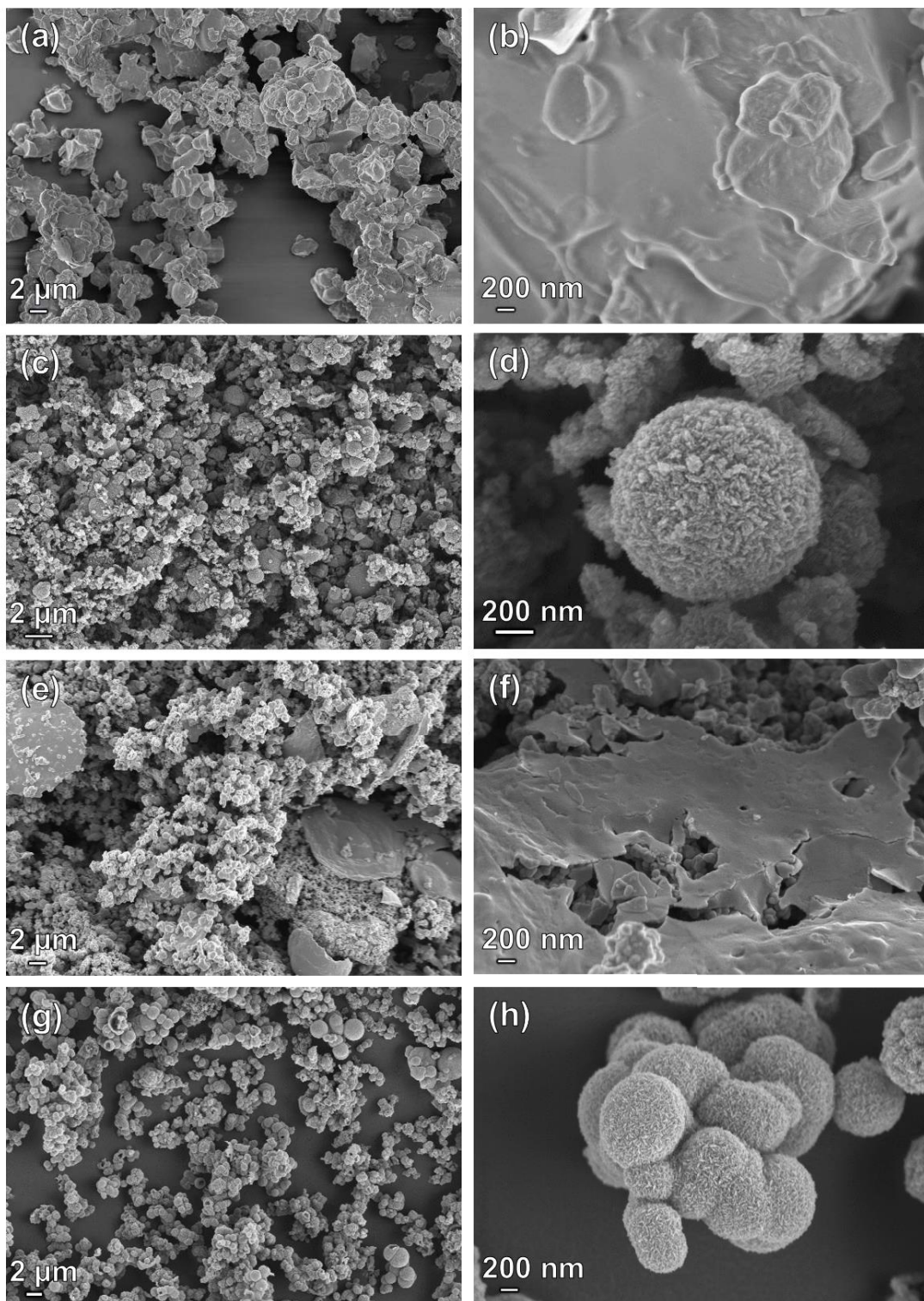


Figure 2. SEM images of the (a, b) $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor, (c, d) hydrothermally treated $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$, called HT- MoO_2/C , (e, f) annealed $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$, called An- MoO_2/C for consistency, and (g, h) annealed hydrothermally treated $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$, called AnHT- MoO_2/C . (a, c, e, g) Low- and (b, d, f, h) high-magnification images are shown.

Figure 2 shows the morphologies of the $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor and the products obtained after hydrothermal treatment and/or annealing. The precursor represents dispersed spherical particles with a rough surface. The shape of the particles suggests that the spheres are coated with foreign material. Less coated particles agree well with the previously reported partial formation of the polydopamine spheres induced by the reaction with hydrogen peroxide.^{16,20} According to the XRD pattern of the $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor (**Figure 3a**), the material on the surface is chemically preintercalated molybdenum oxide with layered structure and dopamine molecules in the interlayer region indicated by the presence of the (00 l) reflections with decreasing intensities as 2θ value increases. Treatment at elevated temperatures drastically changes the morphology of the precursor. After hydrothermal treatment, the spherical shape of the particles is preserved but better defined compared to the precursor particles (**Figure 2c, d**). The diameter of the spheres ranges from 0.4 to 2.5 μm . Some spheres are broken clearly revealing their hollow nature (**Figure S1, Supporting Information**). The surface of the spheres is coated with 20-100 nm thick nanoplatelets. The XRD pattern of the hydrothermally treated $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor corresponds to the monoclinic MoO_2 phase (space group P21/c), a distorted rutile-type structure, consistent with the standard card (JCPDS #73-1249), suggesting that the nanoplatelets are composed of molybdenum dioxide. Annealing of the $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor led to the formation of a material with heterogeneous morphology. **Figure 2e, f** shows a porous network formed by spherical particles 50-500 nm in diameter which are partially coated by the patches of thin sheets. The analysis of the XRD pattern (**Figure 3a**) revealed that the sheets correspond to Mo_2C phase (JCPDS#79-0744) forming on the network of dopamine-derived carbon particles. Therefore, the sample that we called AnMoO_2/C above in fact is $\text{Mo}_2\text{C}/\text{C}$. Annealing of the hydrothermally treated $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor, on the other hand, did not destroy the hollow spheres morphology, as shown in **Figure 2g, h**. Some of the spheres grew together forming conglomerates. Similarly, to the hydrothermally treated material, the spheres are coated with nanoplatelets, however the shape of the platelets is better defined. The diameter of the hollow spheres ranges from 0.4 to 1.5 μm . The surface of the spheres is coated with 50-100 nm thick nanoplatelets. The

coating of nanoplatelets on the AnHT-MoO₂/C looks more uniform in comparison with the sample that was only hydrothermally treated without further annealing. XRD analysis confirms that nanoplatelets correspond to MoO₂ phase (**Figure 3a**). Formation of different molybdenum compounds after annealing of the (Dopa)_xMoO_y@PDopa precursor with and without hydrothermal treatment (MoO₂ and Mo₂C, respectively) indicates an interesting mechanism of interaction between molybdenum, H₂O₂, and dopamine. When the reaction is carried out without dopamine addition, MoO₃ forms²¹ (**Figure S2, Supporting Information**), indicating that dopamine molecules play a dual role. First, they serve as a precursor for carbon formation, and second, their presence in the system leads to the reduction of molybdenum and MoO₂ or Mo₂C formation, depending on the synthesis conditions, instead of compounds with molybdenum in higher oxidation states. Since Mo₂C phase is out of the scope of this work, the following discussion is focused on comparing HT-MoO₂/C and AnHT-MoO₂/C materials.

Transformation of bulky sphere coatings in the precursor into an assembly of nanoplates is in agreement with the presence of dopamine in the interlayer region of molybdenum oxide forming in sol-gel process. The reaction between interlayer dopamine and Mo-O layers leads to the splitting of the bulky coating into nanostructured well-defined platelets, and the process is accompanied by the molybdenum reduction. The presence of dopamine in the interlayer region of the precursor was further confirmed by the FTIR spectroscopy characterization (**Figure 3b**). Adsorption band at 1612 cm⁻¹ is due to N-H bending vibration of primary amine, the band at 1320 cm⁻¹ corresponds to bending vibration of O-H and band at 1242, 1494, and 1448 cm⁻¹ can be assigned to stretching vibration C-O, and C-C on the aromatic ring, and C-N respectively.^{9,13} The small shoulder band at 1710 cm⁻¹ corresponds to the stretching vibration of C=O derived from the oxidation of dopamine.²² While hydrothermally treated and annealed/hydrothermally treated samples don't show these characteristic bands, both have a broad band at 1580/1590 cm⁻¹ and shoulder at 1410 cm⁻¹ which corresponds to N-H vibration with a considerable decrease in the intensity and C-N-C/C-N vibrations.^{9,13}

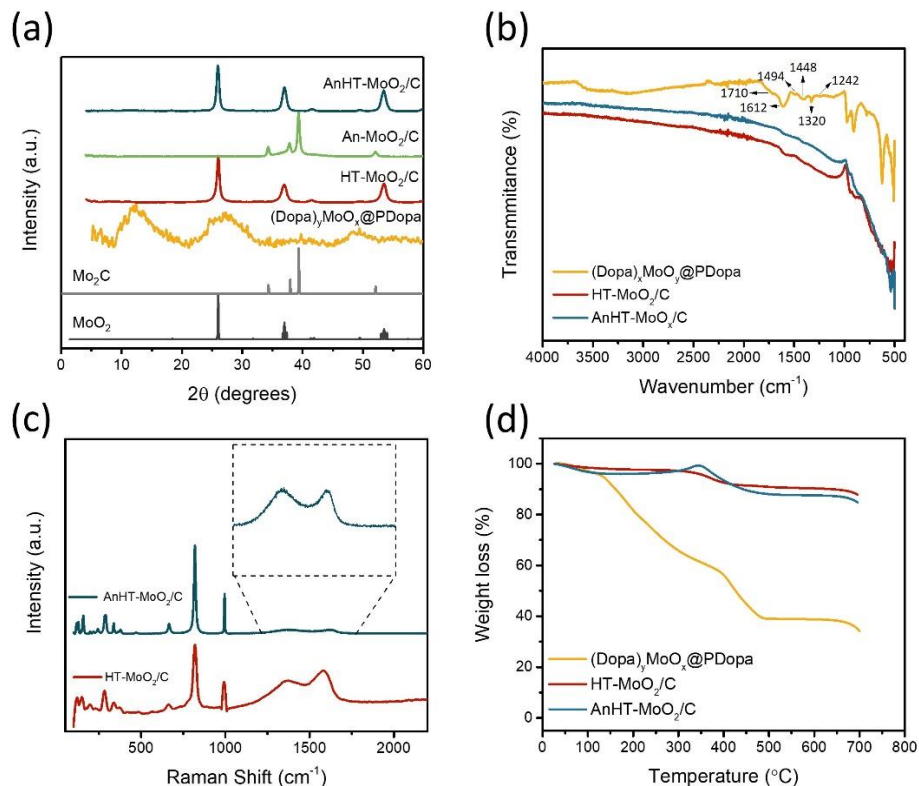


Figure 3. Structural and chemical characteristics of the $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$, HT- MoO_2/C , An- MoO_2/C , and AnHT- MoO_2/C : (a) XRD patterns, (b) FTIR spectra, (c) Raman spectra, and (d) TGA weight loss curves.

Raman spectroscopy measurements confirmed the presence of carbon in the composition of hydrothermally treated and annealed hydrothermally treated $(\text{Dopa})_x\text{MoO}_y@\text{PDopa}$ precursor (**Figure 3c**). The Raman spectra of both samples show two characteristic carbon bands between $1360\text{--}1630\text{ cm}^{-1}$, corresponding to the D and G bands of carbon. For HT- MoO_2/C , D band and G band are observed at 1372 and 1580 cm^{-1} with the I_D/I_G ratio of 0.81 . While for AnHT- MoO_2/C , D and G band peaks are observed at 1368 and 1626 cm^{-1} with the I_D/I_G ratio of 1.06 . Higher intensity for the D band suggests the continuation of carbonization (growth of amorphous carbon) during the annealing treatment.²³ The intense blue shift that is observed for the G band has been previously reported for the transition from graphitic to amorphous carbon.²³ For AnHT- MoO_2/C it is also observed that the G band shift to higher frequencies is accompanied by the broadening of the band and increase in the intensity of the D band.²⁴ It has also been reported that in graphitic carbon materials with a sufficient concentration of defects, the D' band typically positioned at 1620 cm^{-1} can merge with G band inducing the aforementioned shift and the broadening.^{25,26} The bands in the $100\text{--}1100\text{ cm}^{-1}$

region are characteristic of MoO₂. The high intensity peaks at 991, 818, 662, and 282 cm⁻¹ correspond MoO₂ with some degree of surface oxidation.² The low frequency peaks at 120 and 197 cm⁻¹ are indicative of Mo-Mo bending. Therefore, the chemical composition of the synthesized samples is best described as MoO₂/C. However, the Raman spectra suggest that the degree of graphitization in both HT-MoO₂/C and AnHT-MoO₂/C is low.

Thermal stability of the (Dopa)_xMoO_y@PDopa precursor, HT-MoO₂/C and AnHT-MoO₂/C was evaluated via thermogravimetric analysis (TGA) from room temperature to 700°C in air, as shown in **Figure 3d**. The more pronounced weight loss in the case of the precursor corresponds to the large fraction of polydopamine spheres and interlayer dopamine molecules. HT-MoO₂/C and AnHT-MoO₂/C materials showed a more modest weight loss ~15% at 310-700 °C temperature range. Interestingly, for the AnHT-MoO₂/C a slight weight gain is first observed, which corresponds to the oxidation of MoO₂ to MoO₃ occurring at ~320°C. Theoretical mass gain from the conversion of MoO₂ to MoO₃ is reported at 13%,² while mass gain of only 3% suggests simultaneous mass loss due to combustion of the carbon matrix. While the mass gain is reverted for AnHT-MoO₂/C at temperatures above 360 °C.² Eventually MoO₃ sublimates at ~700 °C and becomes airborne (**Figure 3d**).^{2,27} The weight loss corresponds to the carbon transformation into volatile species. The weight loss for HT-MoO₂/C is ~6%, which corresponds to the carbon content of ~18.5 wt. %, taking into account the oxidation of MoO₂. In the case of AnHT-MoO₂/C, the weight loss is ~8%, from which the carbon content was calculated to be ~20 wt. %, taking into account the oxidation of MoO₂. The detailed analysis of TGA weight loss curves is shown in **Supporting Information (Figure S3)**. The four-probe measurements on the films containing 95 wt. % of the active material and 5 wt. % PTFE allowed comparing electronic conductivities of the samples before and after annealing (**Figure S4 and S5 in Supporting Information**). The electronic conductivity of 4.17 KS·cm⁻¹ was calculated for HT-MoO₂/C and 7.83 KS·cm⁻¹ for AnHT-MoO₂/C. A higher value of the electronic conductivity of sample after annealing is in agreement with the higher carbon content found via TGA and carbon with higher degree of amorphization revealed for AnHT-Mo₂/C via Raman spectroscopy characterization.¹⁷

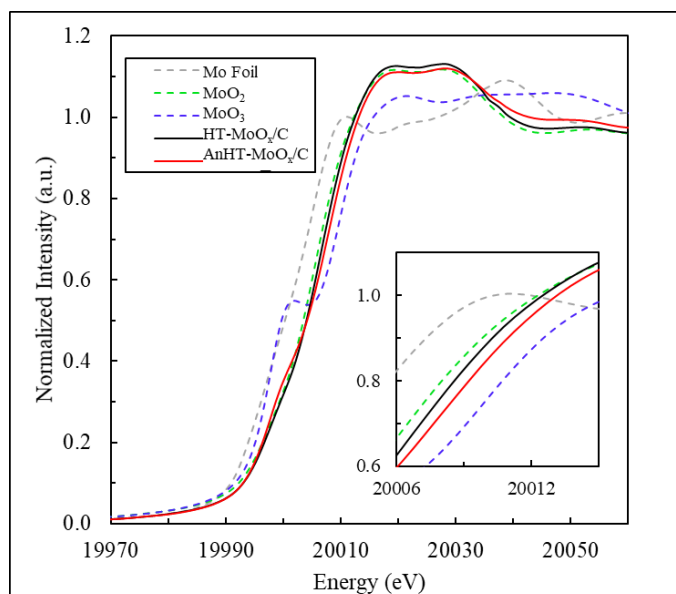


Figure 4. Mo K-edge XANES spectra of the HT-MoO₂/C and AnHT-MoO₂/C. The spectra for the MoO₂ and MoO₃ are shown as a reference.

Table 1. LCF results of XANES spectra of the HT-MoO₂/C and AnHT-MoO₂/C.

Sample	R Factor	Reduced Chi	MoO ₂	MoO ₃	Ox. State	Error
HT-MoO ₂ /C	0.001548	0.000282	94.5% (2.6%)	1.5% (2.6%)	4.0	3.7%
AnHT-MoO ₂ /C	0.002604	0.000441	78.7% (3.3%)	21.3% (3.3%)	4.4	4.6%

The oxidation state of molybdenum centers was determined for two samples, HT-MoO₂/C and AnHT-MoO₂/C via X-ray Absorption Near Edge Spectroscopy (XANES). The XANES spectra of the Mo K-edge were collected for both materials and compared to reference materials that were also measured at the beamline (**Figure 4**). The spectra for the experimental samples closely resemble that of the Mo⁴⁺ standard, MoO₂. Using linear combination fitting (LCF) of the XANES data, the oxidation state of molybdenum for HT-MoO₂/C was determined as 4.0 and that of AnHT-MoO₂/C as 4.4 (**Table 1**).

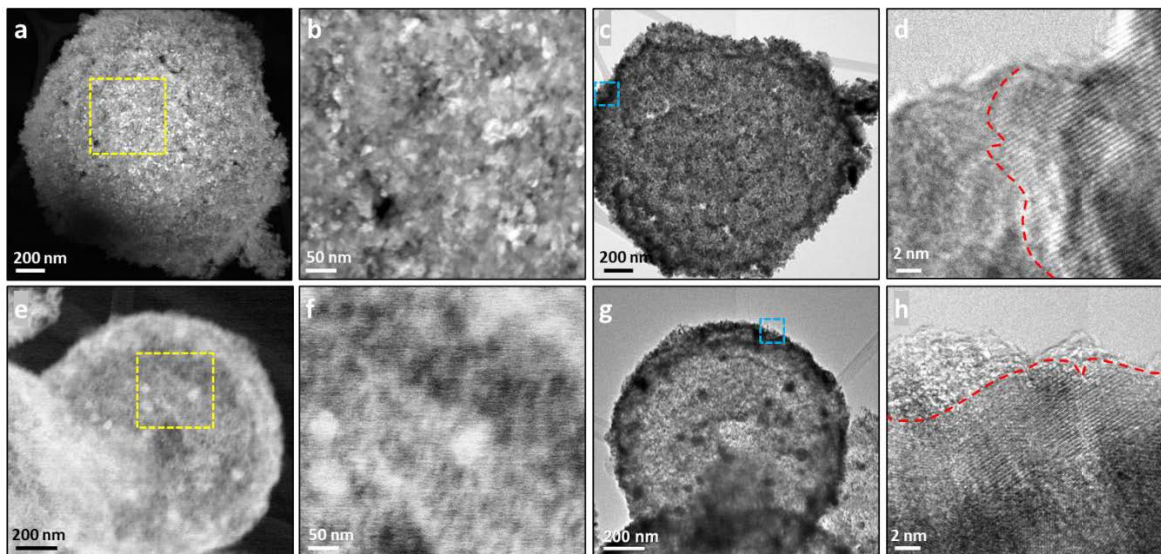


Figure 5. Structural characterization of HT-MoO₂/C (a-d) before and (e-h) after annealing. (a) HAADF-STEM image, (b) HAADF-STEM image with high magnification of the area by the yellow box in (a), (c) TEM image and (d) HRTEM image of the area marked by the blue box in (c) of HT-MoO₂/C. (e) HAADF-STEM image, (f) HAADF-STEM image with high magnification of the are marked by the yellow box in (e), (g) TEM image and (h) HRTEM image of the area marked by the blue box in (g) of AnHT-MoO₂/C.

TEM images of the individual spheres of HT-MoO₂/C and AnHT-MoO₂/C were acquired to gain additional structure information, as shown in **Figure 5**. The HADDF-STEM images (**Figure 5, a-b**) of HT-MoO₂/C show spherical structures comprised of individual nanoplatelets. Around 20% of the imaged sphere contains MoO₂-rich nanoplatelets, as indicated by the brighter area, while the darker area contains a uniform mixture of the dopamine-derived carbon and molybdenum oxide. The TEM image and corresponding HRTEM images confirm the presence of the amorphous carbonaceous component and crystalline MoO₂ (**Figure 5, c-d**). Interestingly, the HADDF-STEM images (**Figure 5, e-f**) of the sample after annealing, AnHT-MoO₂/C, show spherical morphology with a MoO₂-rich shell, and the MoO₂ nanoplatelets are more interconnected to form a porous structure, differing from the structure before annealing. In addition, most of the area of this sphere contains a uniform mixture of carbon and MoO₂ with a small amount of (bright spots, around 5%) MoO₂-rich nanoparticles. From the TEM and corresponding HRTEM (**Figure 5, g-h**), a layer of amorphous carbon coating on the crystalline MoO₂ nanoplatelets was observed. The change in morphology of the spheres confirmed that the annealing treatment has caused further evolution of the MoO₂/C morphology by forming the conductive carbon coating on the individual MoO₂ nanoplatelets and

altering the nanoplatelet assembly to produce a porous shell with more uniform distribution. TEM is in agreement with our conclusion that treatment at elevated temperature does not only result in the carbonization of dopamine but also involves chemical interaction between dopamine and molybdenum compounds. The same interaction is likely to result in the increase of the molybdenum oxidation state after annealing, as revealed by the XANES measurements. Understanding the mechanism of this interaction is outside of the scope of this work and requires a separate study.

The electrochemical performance of the HT-MoO₂/C and AnHT-MoO₂/C electrodes was evaluated in non-aqueous Li-ion systems using coin cells (**Figure 6**). Cyclic voltammetry (CV) profiles are shown in **Figure 6, a, b**. The CV curves for both materials demonstrate two pairs of redox peaks usually indicative of reversible intercalation type behavior. On the first cathodic sweep, the peaks appear at 1.24 V and 1.54 V vs Li/Li⁺, which is attributed to Li⁺ ions insertion accompanied by the monoclinic-orthorhombic-monoclinic phase transformation in Li_xMoO₂.² Li⁺ ions extraction occurs on the anodic sweep indicated by the peaks in CV curves appearing at 1.44 V and 1.72 V vs Li/Li⁺. Higher peak current values, better resolution, and improved reversibility observed in CV curves exhibited by the cells with AnHT-MoO₂/C electrode suggest that structural, compositional, and morphological changes induced by the annealing led to advanced electrochemical activity as compared to HT-MoO₂/C material.

1st, 2nd and 3rd cycle galvanostatic discharge/charge (GDC) curves for the HT-MoO₂/C and AnHT-MoO₂/C electrodes are shown in **Figure 6c** and **d**, respectively. A slightly more narrow potential window of 1.2 – 3.0 V vs Li/Li⁺, compared to CV measurements, was selected to focus on reversible intercalation of Li⁺ ions and exclude the conversion reaction. In fact, when a potential window of 1.0 – 3.0 V vs Li/Li⁺ was used, a more rapid capacity decay was observed with cycling (**Supporting Information, Figure S6**). The tail appearing at potential values below 1.2 V vs Li/Li⁺ was attributed to the beginning of the conversion reaction, which gradually reduces the amount of MoO₂ and leads to the capacity decay in potential window characteristic of the intercalation reaction.

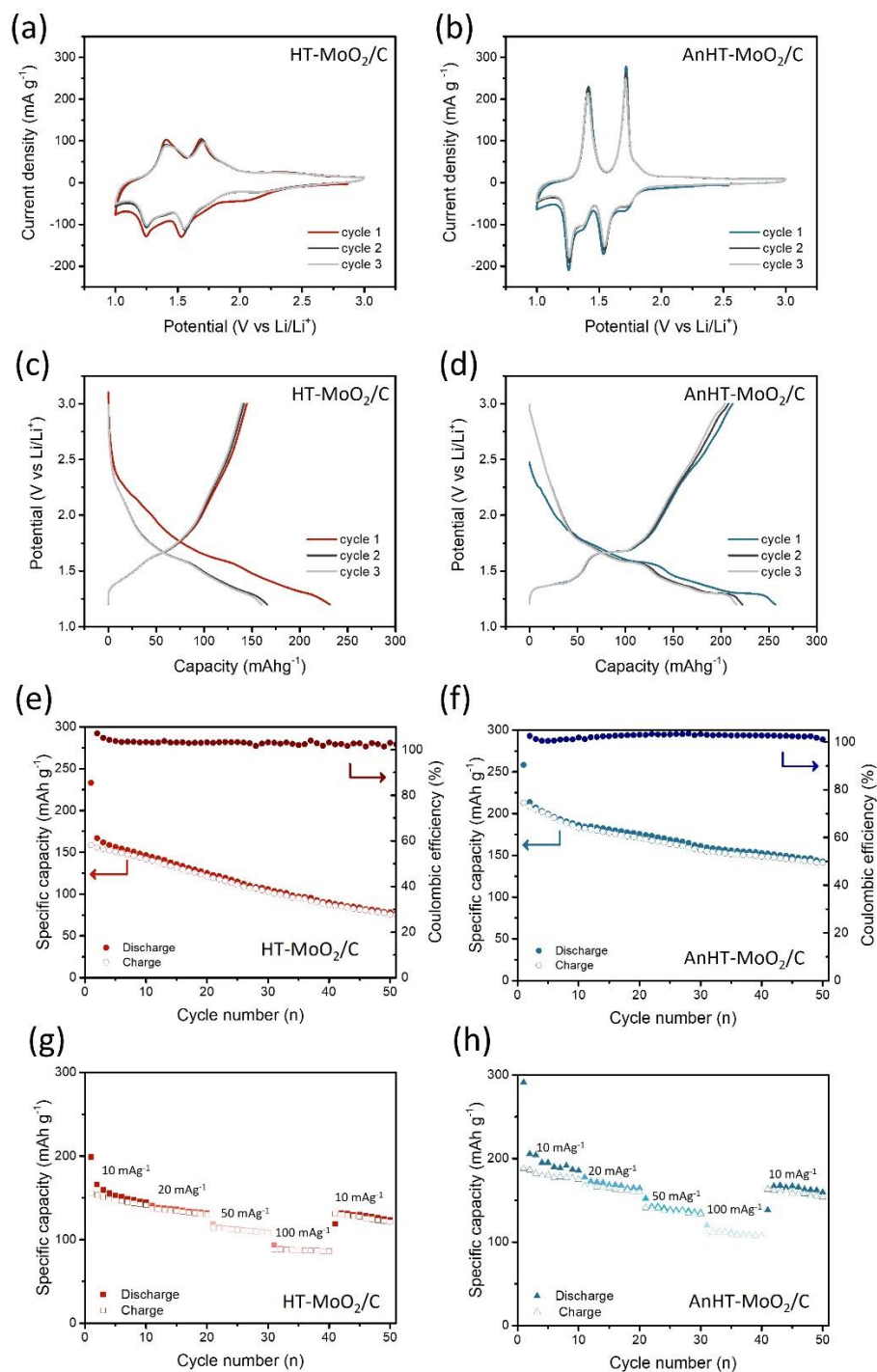


Figure 6. Electrochemical characterization of (a, c, e, and g) HT-MoO₂/C and (b, d, f, and h) AnHT-MoO₂/C electrodes in Li-ion half cells. (a and b) Cyclic voltammograms at a sweep rate of 0.1 mV s⁻¹ in the voltage window of 1.0–3.0 V vs Li/Li⁺. (c and d) First, second and third galvanostatic discharge/charge cycle curves at a current rate of 10 mA g⁻¹. (e and f) Specific discharge/charge capacity and coulombic efficiency as a function of cycle number at a current density of 10 mA g⁻¹ over 50 cycles. (g and h) Rate performance at current densities of 10, 20, 50, 100, and 10 mA g⁻¹. Electrochemical testing shown in panels (c – h) was carried out in the potential window of 1.2–3.0 V vs Li/Li⁺.

HT-MoO₂/C electrode exhibited the first cycle discharge capacity of 235 mAh g⁻¹, while AnHT-MoO₂/C electrode showed the initial specific capacity of 260 mAh g⁻¹ at the current density of 10 mA g⁻¹ corresponding to the current rate of C/20. Higher than theoretical capacity in the first discharge cycle could be caused by solid-electrolyte interphase (SEI) layer formation and minimal contribution from the conversion reaction. The discharge curve shows two plateaus at 1.55 V and 1.30 V vs Li/Li⁺ which agrees with the peaks in the discharge cycle of the CV curves. The GDC curve on the charge cycle shows two plateaus at 1.70 V and 1.42 V, corresponding to the reversible delithiation process (**Figure 6, c, d**). The lithiation and delithiation plateaus in GDC curves of the cells containing HT-MoO₂/C electrodes are less prominent than in case of the cells with AnHT-MoO₂/C electrodes. The capacity drop between the 1st and 2nd cycles is due to the initial dissolution of the active material reported for molybdenum oxide based electrodes.^{5,28} The first-to-second cycle capacity loss for hydrothermally treated sample is more apparent suggesting lower stability of the active material in this sample.

Figure 6 (e, f) shows that improved capacity retention was observed starting from the 2nd cycle onward. After 50 cycles, the HT-MoO₂/C electrode showed a specific discharge capacity of 78 mAh g⁻¹ with a capacity retention of 47%. The AnHT-MoO₂/C electrode exhibited a specific discharge capacity of 142 mAh g⁻¹ with a capacity retention of 67% after 50 cycles. These results clearly demonstrate that improved capacity retention and enhanced Coulombic efficiency were achieved after annealing of the HT-MoO₂/C powder. In the rate capability experiment (**Figure 6g and 6h**), the drops in specific discharge capacity with the step-wise increased current density were evaluated. The HT-MoO₂/C electrode exhibited a specific discharge capacity of 93 mAh g⁻¹ at a current density of 100 mA g⁻¹, corresponding to 56% capacity retention when the current density was changed from 10 to 100 mA g⁻¹. The capacity of 120 mAh g⁻¹ was delivered by the AnHT-MoO₂/C electrode at a current density of 100 mA g⁻¹, corresponding to 86% capacity retention when the current density was changed from 10 to 100 mA g⁻¹. To understand the tolerance of the electrodes to high currents, the current density was brought back to the lowest value of 10 mA g⁻¹ after cycling for ten cycles at each of the selected current densities (**Figure 6, g, h**). The capacity

recovered to an average value of 130 mAh g⁻¹ and 142 mAh g⁻¹ for the HT-MoO₂/C and AnHT-MoO₂/C electrode, respectively. Such behavior indicates that the electrodes remained stable under high current operation conditions.

The improved electrochemical charge storage properties of the AnHT-MoO₂/C electrode, as compared to the HT-MoO₂/C electrode, can be attributed to the higher crystallinity of MoO₂, increased oxidation state of Mo, increased carbon content and carbon properties playing a role in the improved electron transport. The intimate heterointerface between the oxide and carbon components achieved via simultaneous dopamine carbonization and MoO₂ crystallization, combined with the nanostructuring of MoO₂, was crucial to enable efficient charge transfer in the system.

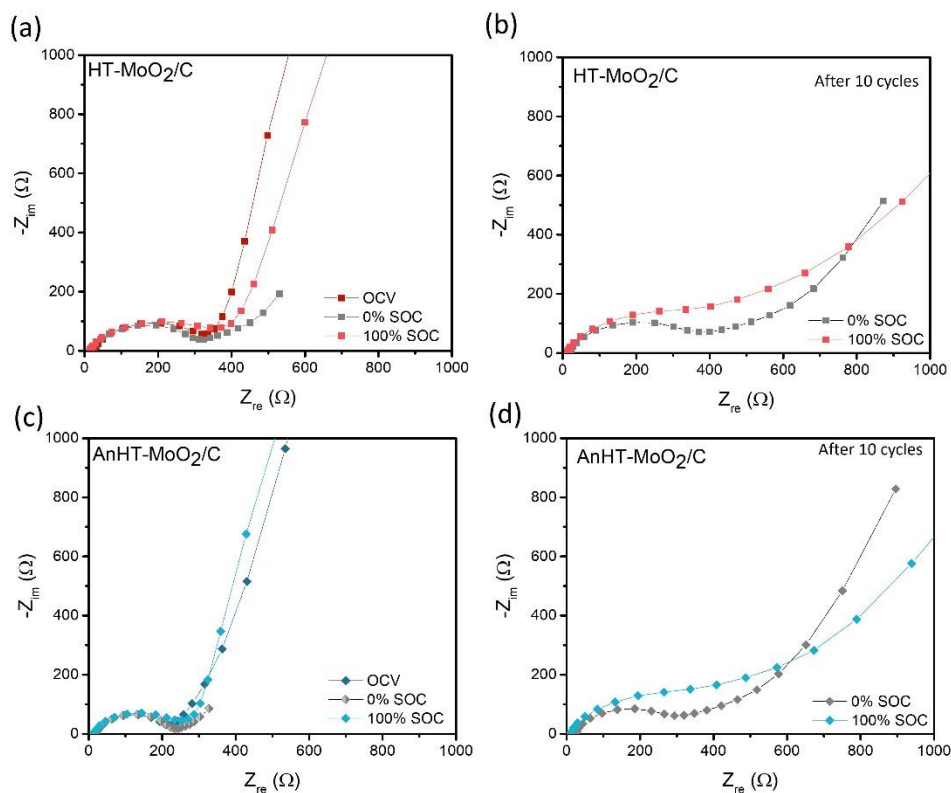


Figure 7. EIS data of the Li-ion cells containing (a, b) HT-MoO₂/C and (c, d) AnHT-MoO₂/C electrodes. (a and c) Nyquist plots at the first discharge/charge cycle at OCV, 0% SOC and 100% SOC at a current density of 10 mA g⁻¹. (c and d) Nyquist plots after 10 discharge/charge cycle at 0% SOC and 100% SOC at a current rate of 10 mA g⁻¹. Electrochemical testing was carried out in the voltage window of 1.2–3.0 V.

Electrochemical impedance spectroscopy (EIS) measurements were carried out to better understand the electrochemical cycling behavior of Li-ion cells containing HT-MoO₂/C and AnHT-MoO₂/C electrodes. **Figure 7** shows the Nyquist plots obtained at OCV, first charge/ discharge cycle and the consecutive charge/discharge cycle after 10 electrochemical Li⁺ ion insertion/extraction cycles. The Nyquist plots show the similar shape of depressed semicircle at medium-to-high frequencies corresponding to the solution and interfacial charge transfer impedance and inclined tail at low frequency attributed to the lithium diffusion impedance. The increase in the resistance after 10 cycles can be traced back to the growth of SEI layer during cycling. Importantly, cells with AnHT-MoO₂/C electrodes show smaller diameter of the semicircles than cells containing HT-MoO₂/C electrodes. This difference is observed for both first and tenth cycles and can be attributed to the improved charge transport capability of the active material and in agreement with the four-probe conductivity measurements. The improved electron transport can be attributed to the improved oxide/carbon heterointerface achieved during the annealing step as revealed by materials characterization. In addition, improved ion transport can be ascribed to the more porous network formed by MoO₂ nanoplatelets and increased oxidation state of molybdenum which are enabled by annealing of the hydrothermally treated MoO₂/C nanocomposite.

5. Conclusion

In this study, hierarchically structured MoO₂/dopamine derived carbon spheres were synthesized for the first time and their charge storage behavior was evaluated in non-aqueous Li-ion system. The integrated MoO₂/carbon structured were prepared using a modified sol-gel synthesis route in which the excess of dopamine molecules led the formation of polydopamine spheres and dopamine preintercalation into the interlayer region of molybdenum oxide. The subsequent processing at elevated temperature, involving hydrothermal treatment (the product was called HT-MoO₂/C) and hydrothermal treatment followed by annealing in the inert atmosphere (the product was called AnHT-MoO₂/C), resulted in simultaneous dopamine carbonization and crystallization of MoO₂ nanoplatelets. The presence of carbon was confirmed

by Raman and FTIR spectroscopy measurements, TGA and imaging. Annealing of the hydrothermally treated material is believed to induce a complex interaction between the molybdenum-derived and dopamine-derived components leading to the increase of the Mo oxidation state, carbon transformation and change in morphology. In this synthesis route, dopamine simultaneously served as carbon precursor and reducing agent leading to the formation of highly integrated structures with tight MoO₂/carbon heterointerface. Electrochemical characterization of the as-synthesized electrodes showed improvements in charge storage properties toward reversible Li⁺ ion intercalation after annealing of the hydrothermally treated material. AnHT-MoO₂/C electrode showed an initial specific discharge capacity of 260 mAh g⁻¹, enhanced capacity retention, and improved rate capability when compared to the hydrothermally treated only HT-MoO₂/C electrode. The superior electrochemical behavior is ascribed to the increased oxidation state of Mo, enhanced stability of MoO₂ nanoplatelets and improved electronic conductivity achieved via annealing in the inert atmosphere. Our work offers a synthetic pathway to create oxide electrodes for intercalation batteries with improved electrochemical charge storage characteristics.

Conventional oxides used as electrodes in energy storage devices suffer from low electronic conductivity, which is currently solved by mixing them with a conductive carbon additive to improve their performance. Physical mixing, however, does not necessarily create a tight oxide/carbon heterointerface. In fact, evolution of the electrode microstructure over extended cycling revealed substantial displacement of the particles.²⁹⁻³¹ Our work shows that a more stable oxide/carbon heterointerface can be created via integration of the oxide precursor with organic compounds followed by treatment at elevated temperatures leading to the carbonization of organics and crystallization of the appropriate oxide phase. The presented synthesis approach is also shown to induce nanostructuring of the oxide phase through the complex interactions with the organic compound. Smaller size of the oxide particles enables shorter ion diffusion distances. Therefore, the oxide/carbon nanocomposites synthesized using approach presented in this work have a potential to exhibit improved rate capability as compared to the physically mixed systems. Moreover, the synthesis method reported in this work for MoO₂ and dopamine can be extended to other oxides and organic

compounds. By exploiting the ability of organic compounds to simultaneously act as a reducing agent and carbon precursor, it is possible to control the oxide phase composition in the structure of the produced oxide/carbon composites and, as a result, their properties. Therefore, the proposed synthesis approach is of interest for a broad range of applications relying on the simultaneous ion and electron transport beyond energy storage, such as sensing and electrochromics.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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